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Taking the plunge: chemical reaction dynamics in liquids

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The dynamics of chemical reactions in liquid solutions are now amenable to direct study using ultrafast laser spectroscopy techniques and advances in computer simulation methods. The surrounding solvent affects the chemical reaction dynamics in numerous ways, which include: (i) formation of complexes between reactants and solvent molecules; (ii) modifications to transition state energies and structures relative to the reactants and products; (iii) coupling between the motions of the reacting molecules and the solvent modes, and exchange of energy; (iv) solvent caging of reactants and products; and (v) structural changes to the solvation shells in response to the changing chemical identity of the solutes, on timescales which may be slower than the reactive events. This article reviews progress in the study of bimolecular chemical reaction dynamics in solution, concentrating on reactions which occur on ground electronic states. It illustrates this progress with reference to recent experimental and computational studies, and considers how the various ways in which a solvent affects the chemical reaction dynamics can be unravelled. Implications are considered for research in fields such as mechanistic synthetic chemistry.



Biography: Andrew Orr-Ewing is Professor of Physical Chemistry at the University of Bristol. He obtained his MA and DPhil degrees from the University of Oxford, the latter under the supervision of Prof G. Hancock. He spent 2 years as a postdoctoral researcher with Prof Richard N. Zare at Stanford University before moving to the University of Bristol in 1994. His

research interests include chemical reaction dynamics in the gas phase and in liquids, molecular photochemistry and photodissociation dynamics, kinetics and mechanisms of reactions of importance in atmospheric chemistry, and cavity ring-down spectroscopy of single aerosol particles. He has received several awards for his research from the Royal Society of Chemistry and was elected as a Fellow of the Royal Society in 2017.

1. Introduction

Complementary experimental and theoretical investigations of isolated reactive collisions provide a wealth of detailed information about the mechanisms of chemical reactions, either in the gas phase or at solid or liquid surfaces.^{1, 2} The experimental studies use low-pressures or molecular beam conditions to avoid further interactions of the nascent products with their surroundings, which otherwise degrade signatures of

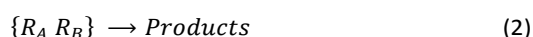
the reaction mechanism. Other articles in this themed issue provide ample illustration of the power of these strategies to unravel the rich dynamics that underlie chemical change. The outcomes have important consequences for our understanding of complex processes in combustion, technological plasmas, the chemistry of planetary atmospheres and interstellar space, and reactions at gas-liquid and gas-solid interfaces, for example during heterogeneous catalysis.

However, many reactive processes of importance in molecular synthesis, biochemistry, the natural environment, and industry require a liquid solvent. A challenge for current research in reaction dynamics is therefore to explore the extent to which ideas derived from the study of isolated collisions can be applied to chemistry in the liquid phase.³⁻⁶ Small clusters of molecules have been used to observe chemical dynamics in environments intermediate between the gas and liquid phases, and are amenable to study by many of the methods developed for gas phase reaction dynamics.^{7, 8} These studies unequivocally provide valuable information about solvation effects under controlled conditions, but the local environments are structurally and dynamically different within a cluster prepared at low temperature (typically a few K) in a molecular beam, and within a bulk liquid at room temperature. Energy transfer and dissipation mechanisms may therefore not be directly comparable. This article reviews some of the methods now available to examine chemical dynamics in bulk liquid solutions directly, and discusses the insights they provide.

Reactions in liquids cannot be considered to occur in isolation because, at the densities typical of the liquid phase, solute molecules interact with the surrounding solvent molecules at intervals typically of a few hundred fs.⁹ The fluctuating solvent bath induces changing solute-solvent intermolecular interactions on timescales comparable to, or shorter than, the

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lifetimes of reactive intermediates and the durations of reactive events. A reaction between reactants R_A and R_B can be represented by a simple mechanism:



Step (1) involves diffusive formation of an encounter pair $\{R_A R_B\}$ within a cage of solvent molecules. Energy transfer from the surrounding liquid must then provide the $\{R_A R_B\}$ pair with sufficient energy to surmount the activation energy barrier to reaction (2), in competition with diffusive separation of R_A and R_B (-1). Products of the reaction equilibrate with the surrounding liquid bath on ultrafast (femtosecond to picosecond) or perhaps longer timescales,^{10, 11} with solute-solvent energy transfer mediated by the fluctuating interactions with the solvent molecules.

This article concentrates on the transformation of $\{R_A R_B\}$ encounter pairs to products, characteristics of the dynamics of this reactive step which can be extracted from observations of the reaction products, and inferences that can be drawn about the dynamical response of the surrounding solvent to the changing chemical identity of the solute. It focuses on bimolecular reactions that occur on the ground electronic potential energy surface (PES). Reactions of excited-state molecules in solution, including electron transfer, proton transfer, isomerization, non-adiabatic internal relaxation, and bond dissociation pathways, have been discussed in several excellent recent reviews and perspective articles,¹²⁻¹⁸ and are not considered further here.

Numerous challenges must be overcome to make incisive experimental measurements of chemical reaction dynamics in solution.³⁻⁵ The ultrafast timescales for reaction, reorganization of the solvent shell, and thermalization of the translational, rotational and vibrational degrees of freedom of the products result in rapid loss of any dynamical signatures of the reaction. Most of the methods developed to infer properties of the PES for isolated, gas-phase reactions, by measurement of scattering distributions and kinetic and internal energies of nascent reaction products,^{1, 2} cannot therefore be exploited. The additional degrees of freedom associated with the surrounding solvent molecules, and the complexity of their couplings to the reacting solute molecules, also present substantial challenges for theoretical descriptions and computational simulations of reaction dynamics in solution. Despite these obstacles, significant progress has been made in understanding the ways in which a liquid solvent affects fundamental reaction mechanisms.^{3, 4}

This review starts by considering how a solvent modifies reaction pathways, and the insights that derive from reaction rate theories which accommodate solvent effects. It then draws on recent examples of experimental and computational research to illustrate the dynamical and mechanistic information that is now accessible for bimolecular reactions in liquids. It concludes with consideration of how this information, and the techniques used, can impact on other fields of chemical research, and challenges that remain to be addressed.

2. How does a solvent affect a chemical reaction?

The rates and dynamics of a chemical reaction are strongly influenced by the relative energies of the reactants, transition state (TS) and products, as well as the location of the TS along the reaction coordinate, and the occurrence of any pre- and post-TS complexes, which are weakly bound by intermolecular interactions.^{1, 2, 19-21} All of these features of a PES for a gas-phase reaction might be modified by immersion in a bulk liquid solvent. The reaction coordinate for an isolated reaction is described by the minimum energy pathway across the PES, linking reactants to products, but in solution account must also be taken of the degrees of freedom of the solvent, giving rise to the concept of a potential of mean force (PMF).²² The PMF is the energy function which describes the average force experienced by the reacting particles at each point along a reaction pathway, and is computed by integration over the distribution of solvent configurations and solute-solvent interactions. It therefore represents a free energy profile for the reaction.

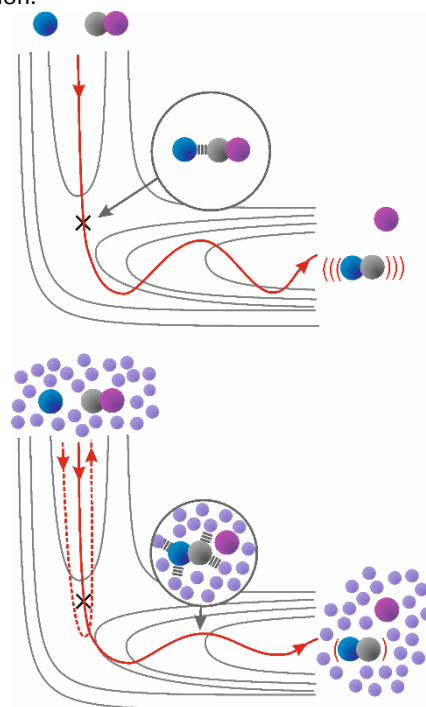


Figure 1: Schematic representation of the effects of a weakly interacting solvent on the chemical reaction dynamics. Top: a gas-phase reaction with an early transition state (x) on the PES produces vibrationally excited products, as indicated by the trajectory shown as a red line. Bottom: a surrounding solvent dampens the product vibrational motions through solute-solvent interactions, shown by dashed grey lines, and can induce re-crossing of the transition state, as illustrated by the dashed red trajectory. The grey contours represent the underlying potential energy surface for the reaction.

In weakly interacting liquid solvents, perturbations to the gas-phase PES caused by solute-solvent interactions are anticipated to be modest. Examples of such solvents are liquid perfluorocarbons and alkanes. The intermolecular interactions that predominate in these non-polar and aprotic solvents are short-range repulsive, and weakly attractive dispersion or induced dipolar forces. Consequently, the reaction dynamics might reasonably be expected to resemble those for gas-phase

reactions, albeit with modifications caused by solvent caging, and frequent solute-solvent collisions, with their associated intermolecular energy transfer. The influence of a weakly interacting solvent on the chemical dynamics is illustrated schematically in **Figure 1**.

More strongly interacting solvents, including those in which polar and hydrogen-bonding intermolecular interactions dominate, will more substantially modify reaction and activation energies. The bulk dielectric constant of the liquid provides some guidance about how the electronic energies of the solute molecules will be perturbed along the reaction pathway. However, explicit account must also be taken of the specific nature of the intermolecular interactions, and of whether the solvent molecules can adjust to their optimum configurations as a chemical reaction takes place in their midst on femtosecond timescales. Indeed, a polar solvent might promote a reaction between charge-separated cations and anions instead of the covalent pathway more characteristic of a gas-phase reaction between the corresponding neutral species. Steady-state infra-red (IR) absorption spectra of solutions can also provide some information about the solute-solvent interactions, for example from the magnitudes of solvent-induced shifts in the centre wavenumbers of fundamental vibrational bands, and through analysis of the band shapes. In the case of small molecules such as HCl dissolved in weakly interacting solvents, residual signatures can be resolved of the well-known P and R-branch rotational structure observed in the gas-phase spectra.^{23–28} The appearance of a sharper feature resembling a Q-branch is an indication of hindered rotation in the solution.^{29, 30}

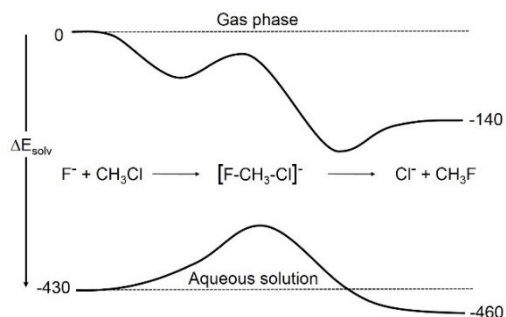


Figure 2: Schematic diagram showing the minimum free energy profiles for the S_N2 reaction of F^- with CH_3Cl in the gas phase (top) and in aqueous solution (bottom). The two curves are displaced by the solvation energy ΔE_{solv} at each point along the reaction pathway. Energies relative to the gas phase reactants are specified in kJ mol^{-1} . The figure is adapted from Ref. [35].

The bimolecular nucleophilic substitution (S_N2) reaction is a textbook example of organic reaction mechanisms, and illustrates how a solvent can drastically modify the energetics of a reaction pathway. **Figure 2** compares the free energy profiles along an S_N2 reaction coordinate for reactions in the gas phase and in aqueous solution and shows dramatic changes to the stabilization of pre- and post-TS complexes and the height of the activation barrier.^{31–34} The effect of the solvent is particularly pronounced for this class of ion-molecule reactions because of the different solvation energies of reactants, products and the transition state. More modest effects are expected for

reactions of neutral species, such as the radical-molecule examples discussed later.

Beyond purely energetic considerations, other influences of the solvent must also be taken into account. The reactants can form complexes with solvent molecules, which change the molecular character of the species participating in a bimolecular reaction.^{36–48} These complexes might be weakly bound, and held together by a solvent cage, or more strongly associated species that diffuse as dimers. The role of complexes is discussed further in Section 3. The surrounding solvent molecules will also exert some stereochemical influence over $\{R_A R_B\}$ encounter pairs and may constrain the geometries of approach to the transition state. Moreover, solvent caging can inhibit separation of products, and therefore can affect the mechanisms of dissipation of energy to the solvent bath.⁴⁹ Under some circumstances, the cage confinement of products encourages re-crossing of the TS back towards reactants.^{50, 51} In effect, the solvent imposes a friction on the reaction which slows the overall rate. The comparative timescales for crossing the transition state region, and for solvent response to chemical changes to the solute molecules, must also be considered because of the consequences for the degree of solvent stabilization of the reaction energy barrier, as is shown schematically in **Figure 3**.

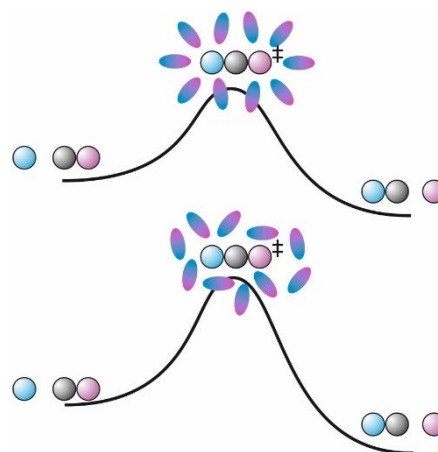


Figure 3: Schematic representation of solvent effects on the height of energy barriers to reactions in solution. Polar solvent molecules are represented by the shaded ellipses. Solvation of the reactants and products is not shown. Top: the solvent response is faster than changes to the nuclear configuration of the reacting species, giving an optimally solvated and stabilized transition state. Bottom: the solvent response is slower than reaction, so the solvent molecules have not adjusted to their most favourable configuration.

In ground-breaking studies, Bergsma *et al.* reported computer simulations of reaction of an atom with a diatomic molecule ($A + BC \rightarrow AB + C$) in a liquefied rare-gas solution.^{52, 53} These studies indicated that the reaction could be conveniently partitioned into three distinct steps: (i) activation of the reactants; (ii) crossing the TS barrier; and (iii) deactivation of excess energy in the products. Steps (i) and (iii) require understanding of energy transfer mechanisms between solvent and solute molecules, whereas step (ii) could be interpreted using the dynamics of the

corresponding gas-phase reaction. When the curvature of the minimum energy pathway across the reaction barrier is low, meaning relatively slow passage of the reaction through the TS region compared with solvent frictional effects, dynamical (i.e. collisional) properties of the solvent induce some TS re-crossings. Fast dissipation of any excess internal energy from the products to the solvent bath^{51, 54} re-establishes thermal equilibrium and inhibits re-crossing of the TS. Benjamin *et al.*⁵⁵ used molecular dynamics (MD) simulations to examine mechanisms of activation of the reagents in an A + BC atom-exchange reaction by energy exchange with the solvent. They observed that one or more solvent atoms / molecules acquire excess energy from fluctuations in the solvent bath, and further collisions transfer this energy to the reactants in the form of the kinetic and rotational energy required to climb the potential energy barrier to the TS.

Transition-state theory (TST) provides a framework to compute rate coefficients for gas-phase reactions,²⁰ but may not be adequate for reactions in solution.⁵¹ In the example above of reactions in a rare-gas solvent, TST provided a good account of the simulated reaction rates except when solvent-induced barrier re-crossings became significant.^{52, 53} This discrepancy arose because TST assumes that reactants with sufficient energy to reach the TS will always form products, an assumption which can be modified by introduction of a transmission coefficient κ ($0 \leq \kappa \leq 1$, with $\kappa = 1$ corresponding to no re-crossing). The observed rate coefficient (k) and the TST prediction (k_{TST}) are connected by $k = \kappa k_{\text{TST}}$. Kramers theory,⁵⁶ and Grote-Hynes theory^{57, 58} provide methods to quantify this transmission coefficient in a fluctuating solvent environment.⁵⁰ In Kramers theory, κ is expressed in terms of the (imaginary) frequency ω associated with a one-dimensional parabolic activation barrier (which is related to the barrier curvature) and the friction coefficient ζ of the solvent (which can be computed from the time correlation function for the random, solvent-induced forces along the reaction coordinate). As the magnitude of the friction increases, κ is reduced from a value of unity, and Kramers theory predicts rate coefficients smaller than k_{TST} .^{50, 53} In addition to deviations from TST caused by solvent-induced barrier re-crossings, Kramers identified that assumptions of thermal equilibrium between the reactants or products and the solvent bath can break down in the limit of low solvent friction, a process which is analogous to the low-pressure regime for rate coefficients in the gas phase.

Kramers theory relies on a description of the molecular motions using the Langevin equation, with instantaneous solvent forces leading to the friction coefficient. This treatment can be inappropriate for reactions of small molecules in a molecular solvent. Barrier crossing times are typically 10 – 100 fs, which constrains the period over which solvent fluctuations can induce barrier re-crossings, and solvent response is not instantaneous in comparison to these ultrafast barrier transit timescales (see bottom panel of Figure 3). This limitation of Kramers theory is addressed in the Grote-Hynes theory of reaction rates in solution,^{57, 58} which incorporates a time-dependent friction coefficient to account for the solvent response during a reaction. This response includes the re-

orientation dynamics of the surrounding solvent molecules towards an optimum arrangement to solvate the reaction intermediates in the vicinity of, and after the TS.^{18, 51}

Advances in the theoretical description of reaction rates in solution⁵¹ include the development of ring-polymer molecular dynamics (RPMD) rate theory,^{59–61} and two recent reviews illustrate applications of RPMD methods to the computation of reaction rates.^{62, 63} The kinetics of diffusion-controlled reactions in solution can be analysed with models based upon Smoluchowski theory,^{64, 65} which consider the survival probability of particles in solution with respect to processes such as radical recombination and bimolecular reaction, while undergoing diffusive motion. These models have been successfully applied to the analysis of experimental data for various reactions in solution.^{9, 39–41, 43, 44, 66, 67}

3. Chemical reaction dynamics in solution

The theoretical methods outlined in Section 2 provide valuable microscopic insights into factors influencing reaction rates in solution, but do not reveal the chemical dynamics at a molecular level because they average over quantum states and degrees of freedom of an ensemble. Instead, molecular dynamics simulations, in which a reactive potential energy surface is embedded in a solvent explicitly treated at the molecular level, can track the dynamical behaviour of individual particles and their interactions during a chemical reaction.^{10, 49, 68–71} The insights obtained are comparable to those forthcoming from quasi-classical trajectory (QCT) calculations on accurate potential energy surfaces for gas-phase and gas-surface reactions. In principle, these MD simulations can also map the flow of any energy released by the reaction as it dissipates to the solvent bath. However, quantitatively correct treatment of the coupling between solute and solvent molecule degrees of freedom remains a challenge.⁶⁹ The quality of these simulations must therefore be established by rigorous tests against experimental measurements. To date, the most detailed and insightful experimental studies of bimolecular chemical reaction dynamics in solution have made use of ultrafast transient absorption spectroscopy. The methodology is described in section 3.1, with illustrative examples presented in sections 3.2 – 3.5.

3.1 Experimental methods for the study of bimolecular reaction dynamics in solution

To catch clear dynamical signatures of a chemical reaction in solution before they are washed out by interactions with the solvent bath, measurements must be made on femtosecond to picosecond timescales. Consequently, experiments most commonly use photoexcitation of the solute or solvent molecules to initiate reaction by homolytic or heterolytic cleavage of a chemical bond, which promptly forms radical or ionic reactive intermediates respectively. The photodissociation of a molecule via a repulsive excited state is generally complete in a few hundred femtoseconds or less, and timescales for bimolecular reactions are then controlled by the delay

associated with encountering a reaction partner, and the need for activation to reach the energy of the transition state. These timescales can be kept to a minimum by working with moderately high concentrations of the reaction partner, or studying reaction with the solvent itself, and by concentrating on reactions with little or no activation energy barrier. For example, for a 1.0 M solution of a co-reactant dissolved in an organic solvent, the co-reactant molecules constitute 5-10% of the liquid. If these molecules are homogeneously distributed, a significant fraction of the radicals formed by photodissociation of a dissolved precursor will have one or more co-reactant molecules in their first solvation shell.

The question then arises of which properties of the reactants and products to measure to obtain information about the chemical dynamics. The rate of loss of reactants can be observed by monitoring characteristic features in their electronic or vibrational spectra, but these measurements generally provide kinetic rather than dynamical information (in the form of exponential decay time constants, or fits to Smoluchowski-type time-dependent concentration expressions). Transient spectra can also reveal the precise nature of the reactive intermediates, which might exist, for example, as complexes with solvent molecules. In favourable cases, the translational and rotational energies of nascent products of unimolecular photodissociation can be measured over short time intervals,^{30, 72, 73} but this information is generally destroyed within a few picoseconds by one or more encounters with the surrounding solvent cage. This rapid dissipation of translational and rotational signatures in the products is likely to prevent their use as diagnostics of bimolecular reaction dynamics, for which the timescale for build-up of products is comparable or greater. Experimental studies have therefore mostly concentrated on the vibrational energy content of reaction products of exothermic chemical reactions, because vibrational excitation of solute molecules can persist over tens or hundreds of picoseconds if the couplings between solute vibrational modes and the solvent bath are weak.^{11, 54, 74-76} These studies are most informative when direct comparisons can be drawn with experimental data for vibrational excitation of the products of the same reaction in the gas phase.⁴ Numerous such examples exist in the literature from the work of Polanyi and others, who analysed infra-red emission from nascent, vibrationally excited products of bimolecular reactions at low pressure in the gas phase to learn about the PESs and dynamics for isolated reactions.⁷⁷

The most successful method to date to study reaction dynamics in solution is transient absorption spectroscopy, which probes the formation and loss of reactive intermediates, and the accumulation of reaction products over time.⁷⁸ The timescales of importance for such studies are typically ~100 fs to 1 ns. Experiments use an actinic pulse to initiate reaction, for example by photodissociation of a precursor to produce reactive free radicals, and a time-delayed probe pulse to observe changes in absorbance, ΔA (or optical density, ΔOD), resulting from the reactions of interest. Changes in the intensity of the probe pulse are measured after transmission through the sample, and are processed using the Beer-Lambert law.⁷⁹

Samples flow through a cell with windows which are transparent at the pump and probe pulse wavelengths. Window separations, and hence optical pathlengths through the sample, are maintained below 1 mm. Broadband UV/visible probe pulses are conveniently generated by focusing the fundamental, second harmonic or third harmonic output of an ultrafast laser into a material such as CaF_2 , and can be extended into the near-IR region.⁸⁰ Difference frequency generation produces mid-IR probe pulses with selected centre wavenumbers, and bandwidths up to $\sim 400 \text{ cm}^{-1}$. Dispersing the frequency components of these UV/visible or mid-IR pulses onto a detector consisting of an array of photosensitive elements provides simultaneous measurements of absorbance over the full bandwidth, with spectral resolution sufficient for most experimental studies in solution.⁷⁹ Instrument response functions of 50 – 100 fs are possible with careful design.^{78, 81}

Transient absorption studies in the UV/visible region are often referred to by the abbreviation TA, with TRIR used to denote time-resolved infra-red absorption measurements. Since both methods rely on transient absorption, some authors prefer to distinguish the type of spectroscopy employed: for example, TEAS and TVAS denote transient electronic absorption spectroscopy and transient vibrational absorption spectroscopy respectively, and will be used here. Analysis of a combination of both TEAS and TVAS measurements can provide an essentially complete kinetic model of the conversion of reactants into products via reactive intermediates, as well as distinguishing the reactivity of free and solvent-complexed radicals.^{43-45, 47, 48, 66, 82-84}

Replacing the actinic, radical-producing excitation pulse with an IR-pump pulse, and retaining the IR-probe can also assist the analysis of time-resolved data by providing independent determinations of vibrational relaxation rates. The resulting time constants are incorporated into kinetic models of production and equilibration of vibrationally excited reaction products as experimental constraints to the fitting of rate coefficients.¹¹ However, care must be taken because the micro-solvation environments, and hence solute-solvent couplings, of newly formed reaction products are often distinct from those of the products at equilibrium in solution. Indeed, reactions have been shown to cause greater perturbation of the solvent environment than IR-excitation.⁸⁵ Time constants for cooling of nascent reaction products may therefore differ from those measured for the same solute molecules initially at equilibrium using IR-pump and IR-probe spectroscopy.⁷⁵ Alternative constraints which can usefully be imposed on the kinetic fits include: (i) ensuring rate coefficients for stepwise relaxation down a ladder of vibrational energy levels comply with expectations for their ratios from Landau-Teller theory,⁵⁴ and (ii) using ratios of transition dipole moments which conform with predictions for a harmonic oscillator to analyse IR-probe absorption band intensities between different vibrational levels.⁸⁶

The higher densities in liquid samples, compared to experiments with gases or molecular beams, make absorption spectroscopy methods feasible, despite their sensitivities being lower than techniques such as fluorescence spectroscopy.

However, some potential problems must be recognized. In particular, absorption by the solvent or co-solutes can mask spectral regions of interest, which is a particular problem for transient IR studies of aqueous solutions because of the broad IR absorption bands of water. Deuteration of solvents can open up the desired spectral windows by shifting the frequencies of the solvent absorption bands, and working with thin samples reduces solvent interferences.

3.2 An overview of experimental studies

The literature on chemical reaction dynamics in solution has evolved considerably over the past decade, but draws inspiration from an early computational study by Benjamin and Wilson,⁸⁷ and pioneering experimental investigations by Hochstrasser.^{88, 89} Benjamin and Wilson proposed photolysis of ICN in solution as a method to study the effect of a solvent on chemical dynamics.⁸⁷ This suggestion was implemented by several researchers who explored the photodissociation of ICN in a range of solvents, as well as the subsequent geminate recombination of I and CN photofragments.^{45, 48, 70, 72, 73, 90-92} The dynamics of these processes have also been subjected to considerable subsequent computational investigation.^{48, 93-95} Raftery *et al.* implemented ICN photolysis as a source of CN radicals for bimolecular reactions and used transient IR absorption spectroscopy to observe HCN and DCN formed following ICN photolysis in chloroform and chloroform-*d*₁ respectively.⁸⁸ These early experiments lacked the time resolution and broadband IR absorption capabilities characteristic of modern studies, but nevertheless provided first evidence of non-thermalized (*i.e.*, vibrationally excited) products from exothermic chemical reactions in solution.

Photolysis of precursors other than ICN provides a range of reactive atomic and radical species, some of which have been exploited in subsequent studies. For example, photodissociation of dissolved Cl₂ produces solvated Cl atoms,⁸⁹ but the reactivity of molecular chlorine towards many organic co-solutes has prompted the use of photolysis of chlorinated organic solvents as an alternative Cl-atom source.^{28, 39-41} Bromine atoms can similarly be produced by photolysis of solvents such as bromoform,^{42, 96, 97} but F-atom production requires other methods because C-F bonds are not readily cleaved by UV light. Dunning *et al.* showed that UV photolysis of XeF₂ liberates F atoms on timescales short enough for bimolecular reaction studies,^{10, 82, 85} but it reacts aggressively with many common organic compounds. Platz and coworkers studied the production of carbenes in solution by photolysis of diazo and diazirene compounds,⁹⁸ and observed reaction with alcohols to make ylide reactive intermediates with zwitterionic character.⁹⁹ Nitrenes can similarly be produced by photolysis of azides.¹⁰⁰ Several studies have explored the photolytic production of thiyl radicals from disulfides and thiols in solution, as well as their recombination and reaction pathways.^{66, 67, 84, 101-108} Prompt photolytic production of cationic or anionic species (for example, for future studies of S_N2 reaction mechanisms) remains difficult, but some examples have been reported.¹⁰⁹⁻¹¹³

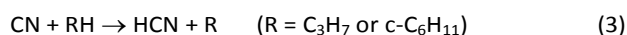
Extensive investigations of the early time photochemistry of alkyl halides in solution have explored formation of atom-solvent molecule complexes, and geminate recombination to higher-energy isomers of the parent molecule (e.g. the *iso*-CCl₃-Cl form of CCl₄, containing a Cl-Cl connectivity), which are suggested to show carbenoid reactivity.^{41, 42, 96, 114-142} Transient absorption bands characteristic of these isomers were also reported in pulsed radiolysis studies of liquids such as CCl₄, but were instead assigned to solvent-separated ion pairs such as CCl₃⁺||Cl⁻.¹⁴³⁻¹⁴⁶ The apparent discrepancies in these assignment were resolved by the calculations of Abou-Chahine *et al.* which showed pronounced ion-pair character of the unusual, higher-energy isomers of carbon tetrachloride and chloroform.⁴¹

Electron photodetachment from dissolved anions is another way to produce neutral radicals for further study. For example, OH (or OD) radicals can be produced in aqueous solution by 202-nm excitation of hydroxide ions to a charge-transfer-to-solvent state.¹⁴⁷ This approach has not yet been applied to studies of bimolecular chemical mechanisms in solution, although interesting OH_(aq) mobility and reaction dynamics have been suggested on the basis of computer simulations.¹⁴⁸⁻¹⁵¹ One further strategy is to convert an unreactive form of a molecule to a reactive isomer photochemically. This approach was implemented by Keiding *et al.*,¹⁵² who photoexcited nitrate (NO₃⁻) ions in aqueous solution to generate peroxyxynitrite (ONOO⁻) ions on a 2 ps timescale. Peroxyxynitrite is a stronger base than nitrate, and the protonation reaction to make peroxyxynitrous acid (ONOOH) was monitored by transient absorption spectroscopy of the ONOO⁻ at 300 nm.

Experimental studies continue to examine the effects of choice of solvent on the observed chemical reaction dynamics. Variation of the microscopic properties of the solvent, such as molecular polarity, protic/aprotic character, and frequencies of vibrational modes, has consequences for the strengths and natures of couplings to the solute molecules, as well as mechanisms for solute-to-solvent energy transfer. Solvents will also influence the dynamics via their macroscopic properties such as viscosity and dielectric constant. The effects of these bulk parameters can be hard to separate from those arising from the microscopic interactions because both are affected by changing the chosen solvent. The consequences of variation of externally controlled parameters such as temperature or applied pressure have also not yet been investigated systematically.

3.3 CN-radical reaction dynamics

Reactions of CN radicals with alkanes are exothermic by more than 100 kJ mol⁻¹, and in the gas phase they produce HCN with considerable vibrational excitation.¹⁵³⁻¹⁵⁹ Glowacki and coworkers carried out QCT calculations for the reactions of CN with propane and cyclohexane,



and accounted for the experimentally observed C-H stretching and H-C≡N bending excitation in terms of the location and

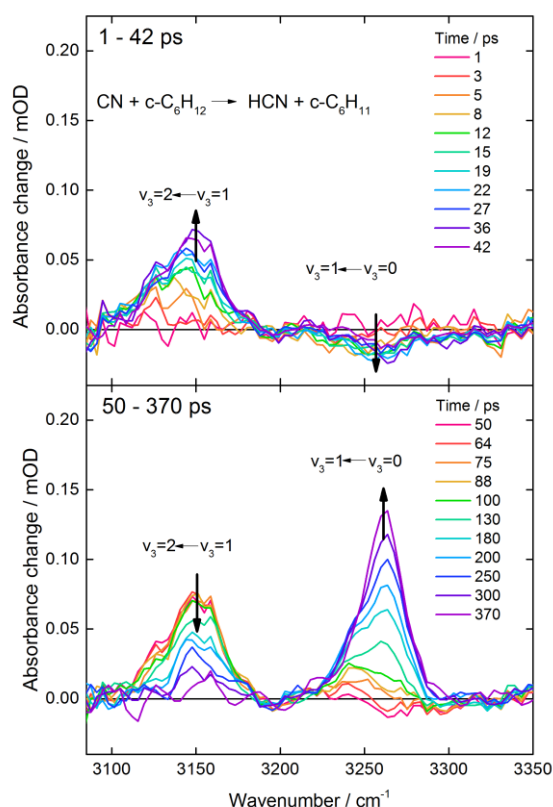
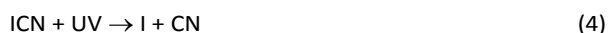


Figure 4: Transient vibrational absorption spectra of the C-H stretching region of HCN formed by reaction of CN radicals with cyclohexane in dichloromethane. Top: time delays from 1–42 ps. Bottom: time delays from 50–370 ps. The inset colour keys provide the delay times for each transient spectrum. Labels above the observed bands identify the anharmonically shifted absorption bands on the C-H stretching (ν_3) mode of HCN from the ground and first excited vibrational levels. Black arrows indicate the directions of change of intensity with time. At later times, absorption is only seen on the $\nu_3 = 1 \leftarrow \nu_3 = 0$ band because of vibrational relaxation in the solvent bath. The shifting of each peak to lower wavenumber with time is indicative of cooling of initial excitation in the bending mode of HCN.

properties of the H-atom abstraction transition state.⁶⁸ The first studies of CN-radical reaction dynamics in solution estimated that only 19% of DCN products from ICN photolysis in chloroform- d_1

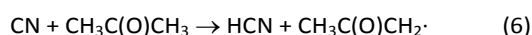


were vibrationally excited in the C-D stretching mode, and that HCN products from similar experiments in CHCl_3 were produced in vibrational thermal equilibrium with the solvent (*i.e.*, in their vibrational ground states). Hochstrasser and coworkers argued that solvent friction effects, or solvent-induced displacement of the TS later along the reaction coordinate, might account for the vibrationally colder products of the reactions in solution.^{51, 88} The role of reactive complexes between CN radicals and solvent molecules was subsequently posited by Crowther *et al.*, on the basis of apparent discrepancies between kinetic data for the loss of CN radical absorption in the near-UV and growth of an HCN absorption band in the mid-IR.^{43, 44} Reaction of a CN radical bound to a solvent molecule by weak intermolecular

interactions could plausibly lead to modifications to the reactive PES characteristic of an isolated CN radical.

More recent TVAS measurements with broadband IR probe pulses provided some remarkable new insights. **Figure 4** illustrates simultaneous observation of the IR bands corresponding to absorption by vibrationally ground state and C-H stretch excited HCN from reaction (3) of CN radicals with cyclohexane in dichloromethane. These and other TVAS measurements demonstrated that the majority of the reaction products of CN with cyclohexane in chlorinated solvents were initially formed with one quantum of excitation in the C-H mode, and up to two quanta of bending excitation.^{11, 92} Indeed, vibrational level population inversions at early times gave net stimulated emission rather than absorption on the fundamental ($\nu = 1 \leftarrow 0$) C-H stretching band in the transient IR spectra of HCN (top panel of Figure 4). This behaviour has since been shown to be general for H-atom abstraction reactions by CN radicals in a variety of solvents, including ones which are more strongly interacting than chloroform and dichloromethane.^{45, 47, 70} Rose *et al.*⁹² and Coulter *et al.*⁴⁵ also presented evidence that the $\text{C}\equiv\text{N}$ stretching

modes of DCN and HCN are vibrationally excited. Their observations suggest that the CN bond is not purely a spectator to the reaction, although intramolecular vibrational redistribution (IVR) from the higher frequency C-D or C-H vibrational modes might contribute to $\text{C}\equiv\text{N}$ stretching excitation. TVAS measurements for the reaction of CN radicals with acetone in CDCl_3 :



demonstrated that *both* the HCN and the 2-oxopropyl radical ($\text{CH}_3\text{C}(\text{O})\text{CH}_2 \cdot$) co-product share the excess energy released by the chemical reaction among their internal vibrational modes.⁴⁷

Delayed onset of the growth of the HCN fundamental absorption bands (in the C-H or $\text{C}\equiv\text{N}$ stretching regions) is a characteristic signature of the initial formation of vibrationally hot products, with the timescales for growth of these bands largely controlled by the rate of vibrational relaxation of the nascent, internally hot HCN products. In weakly interacting solvents such as chloroform and dichloromethane, this vibrational relaxation can take more than 100 ps.¹¹ The relaxation times are strongly solvent dependent, and are also affected by the choice and concentration of a co-reagent.^{45, 70, 83} Experimental measurements by Rose *et al.* of the DCN products of CN radical reactions with cyclohexane- d_{12} in chloroform clearly showed the vibrational cooling of the DCN molecules over time, manifesting as shifts to higher wavenumber of the DCN bands in transient IR spectra.⁹² These shifts are a consequence of the anharmonicity of the vibrational modes. Despite these various observations of internally hot products of reactions in solution, the extent of nascent product vibrational excitation in the gas phase appears to be greater: for example, reactions producing HCN typically show up to two quanta of C-H stretch excitation in the gas phase, but only one quantum of excitation in solution.⁴

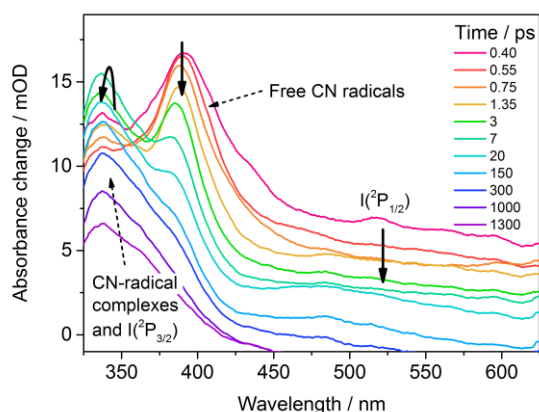
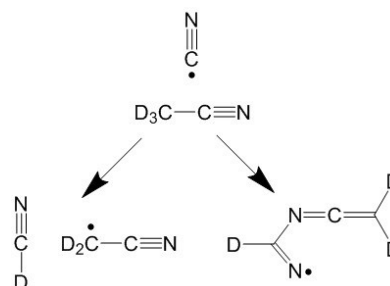


Figure 5: Time-resolved electronic absorption spectra of a solution of ICN in chloroform excited at 267 nm. The inset key identifies the time-delay associated with each transient spectrum. Solid black arrows show the directions of change of various features with time. The sharp feature centred at 390 nm is assigned to the B \leftarrow X absorption band of “free” CN radicals which are only weakly solvated by chloroform. This band evolves into a broader feature peaking to shorter wavelength which has contributions from CN-solvent complexes and a charge-transfer band of $I(^2P_{3/2})$ atoms. Spin-orbit excited $I(^2P_{1/2})$ atoms from ICN photolysis have a corresponding, broad charge-transfer band at longer wavelengths, which is quenched by spin-orbit relaxation.

The picture proposed by Hochstrasser and coworkers of significant modification of the PES by a solvent must therefore be reconsidered. Evidence from the more recent experimental studies, supported by computer simulations with accurate representations of the reaction energetics,^{49, 68, 70} points to only small changes to the location of the TS and the bimolecular reaction dynamics upon solvation in representative organic solvents. However, comparisons between the gas and condensed phase dynamics must consider the role of CN complexes with solvent molecules, which might be stabilized by $\sim 1000\text{ cm}^{-1}$ in solution. These complexes will affect the reaction energetics, and perhaps slightly shift the location of the TS, but were not explicitly included in previous computational simulations. **Figure 5** illustrates the time-dependent changes to the CN radical absorption band observed in TEAS measurements after photolysis of ICN in chloroform. The evidence from these and other such transient spectra is that the newly liberated CN radicals relax into CN-solvent complexes, with illustrative time constants of 0.6 ± 0.1 , 1.1 ± 0.5 and 3.3 ± 1.0 ps in acetonitrile, dichloromethane and chloroform respectively.^{45, 48} In liquid mixtures, such as dilute acetone solutions in chloroform- d_1 , the CN initially complexes to the more abundant CDCl_3 but some radicals exchange the CDCl_3 for an acetone partner when the opportunity arises because the CN-acetone complexes are more strongly bound. The reactive form of CN therefore changes sequentially from free (uncomplexed) CN radicals, to CN- CDCl_3 complexes and then CN-acetone complexes. The evidence from recent reports is that the bimolecular reactions mostly involve the solvent-complexed forms of CN, not the free CN monomers,^{45, 47, 83} because reaction must compete with the short timescales for complex formation. However, the free-CN radical rate coefficients can be significantly larger than those of the solvent-

complexed forms.⁴⁷ The modified reaction dynamics of complexed CN radicals may account for the somewhat lower vibrational excitation of HCN products from reactions in solution compared to the gas phase. However, the possibility also remains of some partial quenching of nascent HCN vibrational excitation in the post-TS region of the reactive PES by coupling to the solvent bath.

The time constant for growth of initial reaction products during reactions of CN radicals with organic co-solutes is determined by the combined rate of all loss processes of the CN radicals. In addition to the bimolecular reaction of interest, these losses include geminate recombination and competing reactions with the solvent, both of which can be observed directly in TVAS measurements. In many of the studies discussed above, deuterated solvents were used in experiments observing HCN production (e.g. from the $\text{CN} + \text{c-C}_6\text{H}_{12}$ reaction), and hydrogenated solvents when DCN was the observed product (e.g. from $\text{CN} + \text{c-C}_6\text{D}_{12}$ reactions). Solvent choices such as these avoid contributions to the HCN or DCN absorption signals from products of reaction with the solvent, but the competing reactions also consume CN and therefore affect measured product formation rates. In some cases, the reactions with the solvent involve very different mechanisms. For example, CN radicals produced by ICN photolysis in acetonitrile solution react by either abstraction of an H atom from the CH_3 group of acetonitrile or competitive addition to the nitrile group (**Scheme 1**), as was revealed by additional bands in the TVAS spectra.⁸³

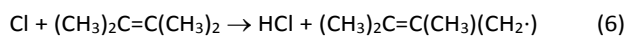


Scheme 1: Competition between D-atom abstraction and addition / rearrangement pathways in reaction of a CN radical with acetonitrile- d_3

3.4 Halogen atom reaction dynamics

Gas-phase reactions of chlorine atoms with various hydrocarbons have been central to the development of an understanding of the reaction dynamics of polyatomic molecules.^{21, 160-173} Translation of such studies into solution has therefore been a priority, and builds on first investigations using transient absorption spectroscopy by Hochstrasser and coworkers.⁸⁹ Sheps *et al.* made extensive measurements of the time constants for loss of Cl atoms and production of HCl product molecules in reactions with a series of organic co-solutes in chlorinated solvents, and analysed the results with Smoluchowski kinetic models.^{39, 40} For reactions with alkanes, the rate coefficients in solution are 10–20 times smaller than the corresponding gas-phase reactions.^{40, 174} First signatures of

vibrational excitation of reaction products came from TVAS measurements by Abou-Chahine *et al.* of the exothermic ($\Delta_r H \approx -80 \text{ kJ mol}^{-1}$)¹⁷² reaction of Cl atoms with 2,3-dimethylbut-2-ene (DMB), in which hydrogen atom abstraction produces a resonance-stabilized allylic hydrocarbon radical.²⁸



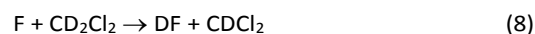
These results were reproduced and extended to more exothermic Cl-atom reactions with unsaturated hydrocarbons by Shin *et al.*¹⁷⁴ The kinetic analyses in these latter two studies distinguished prompt Cl-atom reaction in its immediate solvent cage from diffusive reaction in the bulk, and used numerical fitting to the resulting kinetic equations. The robustness of these numerical fits benefited from independent constraints, such as vibrational relaxation time constants from separate IR-pump and IR-probe measurements, to avoid under-determination of the set of kinetic parameters. The branching to HCl($v=1$) from Cl-atom reaction with 2,3-dimethylbut-2-ene was $15 \pm 2 \%$ in CCl_4 and $24 \pm 4 \%$ in CDCl_3 .^{28, 174} The greater fraction of HCl($v=1$) is observed for the lower viscosity CDCl_3 , suggesting that solvent friction plays a role in damping the HCl vibration in the post-TS region.¹⁷⁴ In both cases, this fraction is significantly smaller than the $48 \pm 6 \%$ reported for thermal reaction of Cl atoms with propene in the gas phase.¹⁷⁵ The disparity between gas and liquid phase dynamics may also reflect the consequences of complexation of reactive Cl atoms with the solvent (the time constants for complex formation are shorter than, or comparable to, the estimated solvent cage escape times),^{28, 41} or coupling of solvent modes to the post-TS region of the PES where vibrational excitation is generated in the nascent HCl.

When Shin *et al.* replaced 2,3-dimethylbut-2-ene by the conjugated diene 2,5-dimethyl-2,4-hexadiene (DMHD), they observed greater branching to HCl($v=1$), with fractions of 23 % and 40 % in CCl_4 and CDCl_3 respectively.¹⁷⁴ The latter reaction is more exothermic ($\Delta_r H \approx -100 \text{ kJ mol}^{-1}$) because of greater conjugation of the radical formed by H-atom abstraction. One quantum of HCl vibration corresponds to a vibrational energy of 34 kJ mol^{-1} , so most of the energy released from either reaction enters degrees of freedom of the solute-solvent system other than HCl vibration. Nevertheless, additional available energy is promoting a higher fraction of vibrationally excited HCl molecules. One possible inference is an earlier TS in the Cl + DMHD reaction than the Cl + DMB reaction, although calculations by Shin *et al.* found no evidence for this change.¹⁷⁴ In these reactions of Cl atoms with unsaturated hydrocarbons, Cl-atom addition to a C=C bond competes with allylic H-atom abstraction from a methyl group. In the gas phase, under low pressure conditions, chloroalkyl radical adducts will undergo unimolecular decomposition to eliminate HCl,¹⁷⁰ but in solution the adducts are stabilized by energy transfer to the solvent bath. No evidence was reported from the TVAS studies for the accumulation of chloroalkyl radicals, and the observation of HCl products indicates that the direct abstraction dynamics remain competitive.

Fluorine atom reactions with hydride molecules have also proved pivotal in the development of a profound understanding

of chemical reaction dynamics.¹⁷⁶⁻¹⁸⁴ Experimental studies of gas phase reactions extracted information as detailed as product-pair correlated vibrational energies, the signatures of quantum reactive scattering resonances, and frequencies of quasi-bound motions in the vicinities of the reaction transition states. The reactions are highly exothermic, and known to produce vibrationally excited HF (or DF) in the gas phase, so appear well suited to complementary studies in solution. The main obstacle to overcome was to find a convenient photolytic source of F atoms, and Dunning *et al.* selected and characterized XeF_2 photolysis⁸² on the basis of prior nanosecond flash-photolysis studies by Bucher and Scaiano.¹⁸⁵

The absorption bands of HF and DF in solution are substantially inhomogeneously broadened, because the vibrational frequencies are sensitive to the local solvation environment. The extent of broadening is such that there is overlap between anharmonically shifted IR bands corresponding to the $v=1 \leftarrow v=0$, $v=2 \leftarrow v=1$ and $v=3 \leftarrow v=2$ absorptions. Nevertheless, the production of vibrationally excited DF molecules was observed from reactions of F atoms with solvents CD_3CN and CD_2Cl_2 (for which $\Delta_r H \approx -150 \text{ kJ mol}^{-1}$),



by making use of the full bandwidth of an ultrafast IR laser pulse.¹⁰ Similar outcomes were subsequently reported for the HF products of reaction of F atoms in liquid CH_3CN .⁸⁵ In CD_3CN , 55% of the DF was deduced to form in $v=2$, and 44% in $v=1$, with 15% uncertainty, and vibrational relaxation time constants were a few ps. In CD_2Cl_2 the branching fractions to $v=2$ and 1 were 77% and 22%, with 11% uncertainty. The channelling of part of the available energy into DF vibrational modes is a striking signature of the reaction dynamics, but the degree of nascent product excitation is greater in the gas phase.^{186, 187} Again, the liquid-phase studies indicate solvent-induced damping of the nuclear dynamics of the reacting species which cause the product vibrational excitation.

Computer simulations by Glowacki and coworkers, using an accurate energy surface for the solvent-coupled F + acetonitrile reaction and dynamics simulated in a box of 100 explicit solvent molecules, captured most of the experimentally observed behaviour.^{10, 69} Snapshots of a representative reactive trajectory are shown in **Figure 6**. The simulations also revealed several elegant mechanistic insights: for example, at early times there is almost unhindered rotation of the newly formed and vibrationally hot DF molecule in a cavity in the solvent, followed by formation of the first hydrogen bond between this DF and a neighbouring solvent molecule (on timescales too short to be experimentally resolved).^{10, 69} These results are all the more notable because of the expected strong interactions between acetonitrile solvent molecules and the reacting species. At the earliest times after DF formation, solvent molecules are not optimally oriented to solvate this product and must reconfigure on sub-ps timescales. The experiments also observed a shift of the DF or HF absorption bands to lower wavenumber over timescales of 5–30 ps, which was attributed

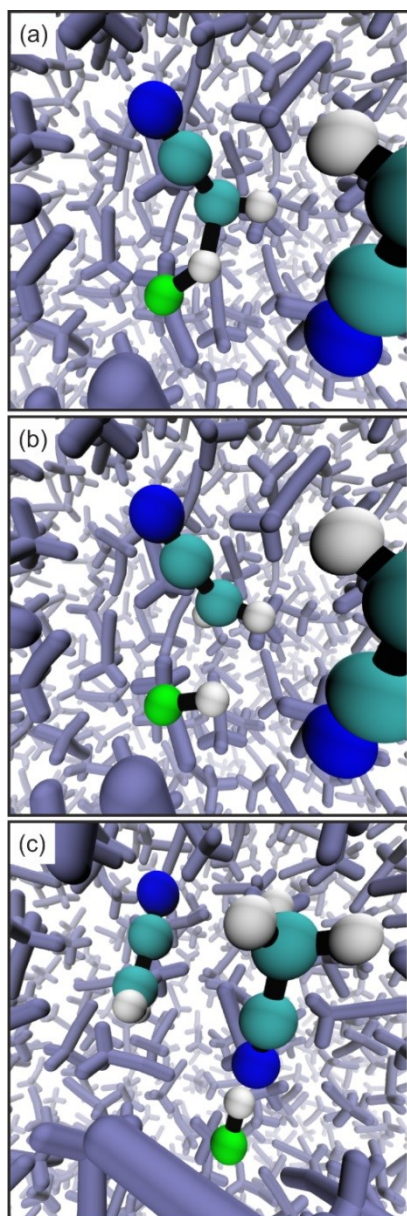


Figure 6: The early time dynamics of a newly formed DF molecule, captured from a computer simulation of reactions of F atoms (bright green) in acetonitrile- d_3 . The DF is formed by reaction of an F atom with a CD_3CN solvent molecule, and panel (a) corresponds to the point at which the D-atom is abstracted. After 130 fs, panel (b) shows nascent DF and CD_2CN reaction products. The DF is able to rotate almost unhindered in a cavity in the surrounding solvent. Panel (c) contains a snapshot after 760 fs, by which time the DF has established a hydrogen bond with a nearby solvent molecule. The images used to make this figure were created by Dr David R. Glowacki, University of Bristol.

to further restructuring of the surrounding solvent environment to accommodate the new reaction products, exchange of hydrogen bonding partners,¹⁸⁸ and dissipation of the heat released by the exothermic reaction from the immediately surrounding solvent shells into the bulk solvent.

Br and I atom reactions with hydrocarbons to produce HBr or HI are generally endothermic, and therefore not considered attractive choices for gas or liquid phase studies. However, Case and coworkers exploited the endothermicity of the Br atom reactions in a recent study which provides first evidence that

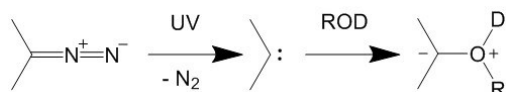
reactions in solution can be promoted by vibrational excitation.⁹⁷ The loss of photolytically generated Br atoms in methanol or dimethylsulfoxide (DMSO) was induced when an ultrafast near-IR laser pulse excited the first overtones of C-H or O-H stretches in the solvent molecules. Near-IR enhanced pH changes in the samples indicated greater HBr yields when the solvent molecules were vibrationally excited. These outcomes are remarkable because they suggest that vibrationally promoted endothermic reactions can compete with the fast vibrational cooling of the near-IR excited solvent molecules, perhaps offering routes to vibrational control of reactivity in solution.

3.5 Reactions of ions, carbenes, and organic radicals

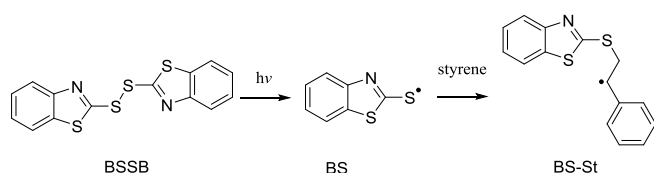
Experimental studies of the ultrafast reaction dynamics of cationic and anionic species remain rare. The protonation of aqueous $ONOO^-$ was mentioned earlier,¹⁵² and a further example involves the photolytic production of benzhydryl cations. Riedle and coworkers were able to produce these carbocations on ultrafast timescales by UV photolysis of benzhydryl triarylphosphonium salts ($R_2CH-PR'_3X^-$ with R and R' denoting aryl groups and $X^- = BF_4^-, SbF_6^-$).^{110, 113} The R_2CH^+ cations have distinctive absorption bands at visible wavelengths which permit their observation by TEAS, and they are removed by reaction with the solvent, the counter anion X^- , or the PR'_3 leaving group. A combination of transient absorption spectroscopy and molecular dynamics calculations again provided key mechanistic insights.¹¹¹ The cation relaxes into a planar geometry within a few hundred fs, with accompanying changes to the surrounding solvent. In the presence of an alcohol, nucleophilic attack at the electrophilic cation produces an ether on timescales of a few picoseconds. R_2CH^+ production by UV photolysis of R_2CHX ($X = Cl$ or Br) was also examined.¹¹² Close interrogation of the short-time dynamics indicated that the initial bond cleavage is mostly homolytic, making contact $R_2CH\cdot + X\cdot$ radical pairs; cation formation then results from electron transfer between closely spaced radical pairs, which is energetically favourable in polar solvents such as acetonitrile. Direct formation of cation and anion pairs may also occur in other organohalide molecules via dissociative dynamics on ion-pair excited states which are stabilized in polar solvents.^{109, 189, 190}

Carbenes (R_2C species with two unshared valence electrons, adopting triplet and singlet forms) can be conveniently prepared in solution by photolysis of diazo and diazirene compounds, but ultrafast dynamics studies have focused mostly on their production, intersystem crossing, and unimolecular rearrangement reactions.^{98, 191-205} A few examples of bimolecular interactions and reactions have been reported. For example, Platz and coworkers observed shifts to longer wavelength in the electronic absorption spectra of p-biphenyltrifluoromethyl carbene in coordinating solvents such as alcohols, which they attributed to reorganization of the solvent molecules to interact with the empty and doubly occupied orbitals on the carbene carbon atom.²⁰⁶ Xue *et al.* subsequently reported direct observation of the carbene-

alcohol ylide (a zwitterionic $RR'C-O^+DR''$ reactive intermediate species) formed by reaction of carboethoxycarbene with CH_3OD (see **scheme 2**).⁹⁹ Transient IR spectra revealed ylide formation within 2 ps, suggested to be from reaction of the nascent, vibrationally hot carbene produced by photolysis of a diazo precursor. The ylide absorption bands narrowed and shifted to higher wavenumber over 6 ps, indicating that the ylides were also formed with excess vibrational energy which dissipates rapidly to the solvent. Similar behaviour was seen for nitrile and ether ylides formed by reaction of the carbene with acetonitrile and tetrahydrofuran, respectively.



Scheme 2: Photolysis of a diazo compound to form a carbene, and reaction with a (deuterated) alcohol to produce a zwitterionic ylide.



Scheme 3: Photolysis of BSSB and reaction of BS radicals with styrene.

The carbocations formed by proton transfer from an alcohol solvent to a carbene have also been observed by ultrafast transient spectroscopy.^{191, 207, 208} Knorr *et al.* recently revisited the reaction dynamics of carbenes in mixed alcohol / acetonitrile solutions in a study combining ultrafast transient absorption spectroscopy and quantum mechanics/molecular mechanics (QM/MM) simulations.²⁰⁹ Their investigation highlighted the dynamical roles played both by a methanol molecule (MeOH) directly H-bonded to the carbene, and by one or more secondary MeOH molecules solvating this coordinated MeOH, in triggering the proton transfer to the carbene centre which ultimately leads to an ether product.

Bimolecular reactions of organic radicals in solution can also be followed on picosecond to nanosecond timescales by transient absorption spectroscopy. For example, Koyama and Orr-Ewing used UV photolysis of the disulfide compound 2,2'-dithiobis(benzothiazole) (BSSB) as a source of benzothiazole-2-thiyl (BS) radicals, and observed their addition reactions with the C=C bond in styrene (**Scheme 3**), an example of a thiol-ene reaction.⁶⁶ A combination of TEAS and TVAS measurements tracked the formation of the BS radicals, identified the reactive intermediates and products involved in the radical addition reaction, and determined rate coefficients for the sequential reaction steps. **Figure 7** shows representative TVAS data for reaction of BS radicals with styrene and highlights the simultaneous observation of several participating species.

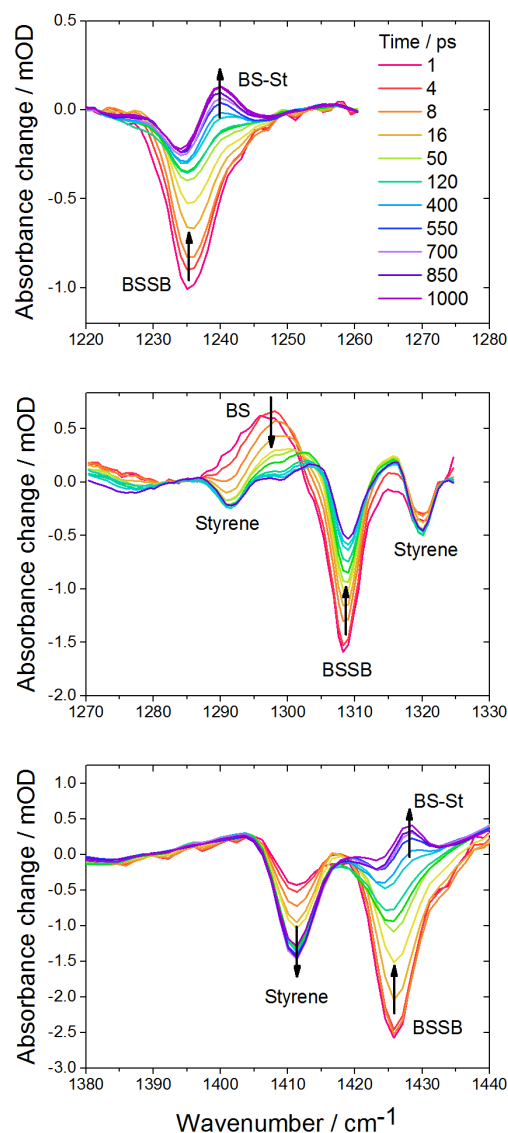
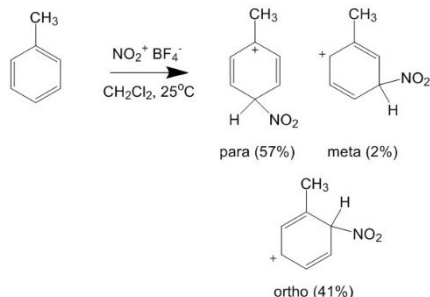


Figure 7: Time-resolved vibrational spectra showing reaction of photolytically generated BS radicals with styrene. BSSB is the parent disulfide photolysed at 330 nm to produce BS radicals, and BS-St is the product of addition of a BS radical to the C=C olefinic bond in styrene. The BSSB concentration is depleted by the photolysis, giving negative-going, bleach features which recover because of geminate recombination of BS radical pairs. The additional bleach features assigned to styrene grow in magnitude with time because styrene is reacting to make BS-St.

These types of spectroscopic observation can be extended from sub-picosecond to microsecond time intervals in a continuous set of measurements using new laser system designs.²¹⁰ Studies using such lasers, and spanning more than 7 orders of magnitude of time, are now able to observe several sequential steps in photoinitiated reactions, starting with the ultrafast production of reactive radicals.⁸⁴

4. Bridging the gap to chemical synthesis

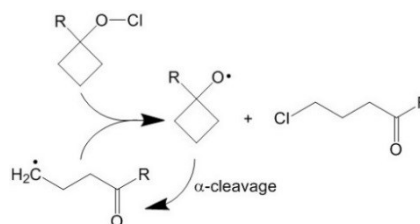
One objective of the field of reaction dynamics is to develop a deep understanding of reaction mechanisms, which can be used to inform research in other disciplines. This aim is already being met in fields such as atmospheric and combustion science, but the impact is not yet as significant in chemical synthesis. Nevertheless, progress is being made, as this section illustrates.



Scheme 4: Nitration of toluene by nitronium ion (NO_2^+) and the experimentally determined branching ratios to para, meta and ortho adducts.

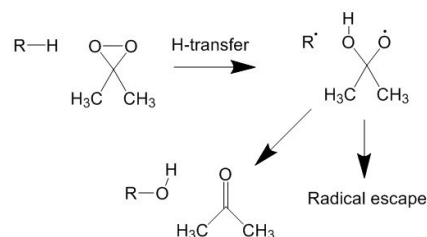
Trajectory calculation simulations of organic reactions in solution have revealed some profound mechanistic insights,^{211–217} and resolved long-standing questions about reaction regioselectivity. For example, Nieves-Quinones and Singleton used direct dynamics trajectory calculations to show that the regioselectivity of nitration of toluene by a nitronium (NO_2^+) ion (**Scheme 4**) can only be accounted for with explicit treatment of the reorganization of the surrounding solvent molecules and the counter-ion (in this case, BF_4^-).²¹⁵ Alternative arguments based on the locations and structures of intermediates and transition states for the competing reaction pathways fail because the reaction pathways bifurcate (or multifurcate) to different products after a single TS. A dynamical treatment in which the reactants and solvent molecules explore a free energy surface is therefore required to resolve this long-standing question about product branching ratios.

Singleton and coworkers also identified cases in which non-thermalized vibrational content of reaction intermediates promotes further reaction: the ring-opening of cycloalkyl hypochlorites to make chloroalkylketones proceeds by a radical-mediated cycle in which a Cl atom is transferred from the hypochlorite moiety (**Scheme 5**).²¹⁴ The subsequent α -cleavage ring-opening of a cyclic alkoxy radical over an energy barrier is favoured for the internally hot radicals which are generated by the early TS for the exothermic Cl-atom transfer step. This excess internal energy is non-statistically distributed, and the concentration of energy in the cyclic part of the molecule ensures the ring-opening step out-competes intramolecular vibrational redistribution and vibrational energy transfer to the solvent.



Scheme 5: Ring-opening reaction of a cyclobutyl hypochlorite to a chlorobutyl ketone via radical intermediates.

The bimolecular reaction of dimethyldioxirane ($(\text{CH}_3)_2\text{CO}_2$) with isobutane involves an initial H-atom transfer to form a radical pair, and provides a further example of solvent-induced changes to reaction pathways. Houk and coworkers carried out direct dynamics trajectory calculations to show that while only 10% of these radical pairs undergo a subsequent OH-transfer reaction to make t-butanol and acetone in the gas phase, this fraction becomes 90% in acetone solution (as modelled using an implicit solvent).²¹⁷ The reaction is illustrated in **Scheme 6**. The radical pair has a lifetime of <150 fs before either separating or undergoing the second reaction step, and the free energy profile for this further reaction becomes barrierless in the acetone solution. The choice of an implicit, continuum treatment for the solvent reveals the effect of solvent polarity on the reaction dynamics, but does not incorporate explicit interactions between solvent and solute molecules. It therefore does not account for steric hindrance in the solvent cage, or for solvent reorientation and relaxation, although the dynamics of the latter processes are likely to be slower than the <150 fs loss of the radical pair.



Scheme 6: Reaction of dimethyl dioxirane with isobutane to produce acetone and t-butanol ($\text{R} = (\text{CH}_3)_3\text{C}$).

In examples such as those described above, the trajectory calculation results were contrasted with predictions from statistical rate theories and with asymptotic experimental outcomes such as product branching ratios. The use of ultrafast spectroscopy to observe directly the reaction intermediates and solvent effects responsible for product selectivity remains largely untested, but could provide critical validation of these predicted non-statistical dynamics of organic reaction mechanisms in solution.

Further opportunities undoubtedly lie in wider applications of transient spectroscopy techniques for the study of reactive intermediates.²¹⁶ These elusive species survive for only tiny fractions of a second, and therefore cannot be isolated for

analysis by traditional means. The ultrafast transient absorption spectroscopy techniques which are central to the advances described in this review are poised to make increasingly important contributions to mechanistic understanding of organic and inorganic chemistry. Some examples are presented in Section 3.5, and others will be forthcoming as the power of a combination of TEAS and TVAS methods is more widely recognized. As was mentioned earlier, methods are now available for observation of reactive sequences over many orders of magnitude of time,^{210, 218} from femtosecond to millisecond regimes. This capability will allow detailed reactive pathways to be mapped, and first examples are now emerging.⁸⁴ The mechanisms of other widely used synthetic procedures, such as photoredox catalysis, are attractive targets for future study.

Some well-known chemical reactions still evade detailed experimental study of their dynamics in solution. A prominent example is the S_N2 reaction mechanism, for which theoretical modelling and computer simulation have a long history,^{219–222} and remain far ahead of condensed phase experimental studies,^{33, 34} although gas-phase experiments and simulations have characterized the isolated bimolecular dynamics and the effects of microsolvation in clusters.^{223–226} Future breakthroughs in liquid phase dynamics experiments require prompt and efficient sources of anions and cations for study of S_N2 and other ion-molecule reaction mechanisms.

5. Future directions and challenges

Numerous challenges remain for the characterization of the dynamics of bimolecular reactions in solution. One ambition is to provide a full description of how solvent molecules couple to a reaction coordinate and modify the reaction as it is occurring. Intermolecular interactions specific to the solute and solvent molecular structures (such as hydrogen bonding), short-range impulsive (collisional) couplings, Förster-type couplings (which depend on the spectral overlap of solvent and reacting solute modes), and solvent viscosity might all contribute to the effective solvent friction which damps the motions of the reacting species. A complete experiment should strive to observe these reactant nuclear dynamics, the time-dependent response of the neighbouring solvent molecules, and the flow of energy into the products and their surroundings. This level of observation remains far off in experiments, but is becoming tractable for accurate computer simulations. Ultrafast X-ray scattering,^{227, 228} THz spectroscopy,^{229, 230} and coherent two-dimensional spectroscopies^{86, 231} may be techniques which can resolve the real-time solvent response around a chemical reaction.

A number of further questions remain to be addressed. For example, several of the studies of exothermic reactions described in section 3 reveal that nascent products have high internal energies, and that establishing local thermal equilibrium (LTE) can take tens or hundreds of picoseconds. It remains to be seen whether these non-LTE conditions can be exploited to promote further reactions, but some evidence

from computer simulations suggests this might be possible.^{216, 232, 233}

Experimental TVAS studies of reactions in water are problematic because of the strong absorption of this solvent across the mid-IR range. Windowless, wire-guided flowing jets of aqueous solutions can produce stable films only 6 – 100 μm thick,²³⁴ allowing ultrafast spectroscopy experiments with reduced background contributions from the water, but transient absorption signals also become weak over these short pathlengths. Alternatively, ultrafast stimulated Raman spectroscopy methods can circumvent the problems associated with mid-IR water absorption bands.²³⁵

Other solvents of technological interest, but which have not yet been employed in liquid-phase chemical reaction dynamics studies, include supercritical fluids and ionic liquids. Certain very weakly interacting solvents, such as perfluorocarbons or liquefied rare gases, provide solvation environments that are intermediate between liquid and gas phases.^{75, 236} Translational, rotational and vibrational signatures of nascent reaction products might be observable in these solvents,³⁰ allowing different solvent influences on the reaction dynamics to be isolated. In mixed solvent environments, such as in ternary sample mixtures, the distributions of the components may not be spatially homogeneous, and specific microsolvation environments around the reactants could influence the chemical dynamics. Methods to probe inhomogeneities in the microscopic solvent structure are therefore required.

Conclusions

A combination of ultrafast laser spectroscopy measurements and computer simulations now offers an in-depth understanding of the factors influencing chemical reaction dynamics in solution. The timescales for reactants to pass through the transition state region are comparable to, or shorter than those for the surrounding solvent molecules to respond. The chemical dynamics can appear similar to those for isolated reactive collisions in the gas-phase, even under circumstances of strong interactions of the solvent with the reacting solutes, if the solvent molecules are effectively frozen in position during a fast reaction. In this regime, the solvent molecules do not re-orient to solvate optimally the reacting species at all points along the reaction coordinate. Clear signatures of these gas-phase like dynamics are observed in liquid-phase studies of exothermic H(D)-atom abstraction reactions, including those of CN radicals with various organic molecules, F-atoms with CD_3CN and CD_2Cl_2 , and Cl-atoms with unsaturated hydrocarbons, all of which produce vibrationally excited reaction products. However, the degree of product vibrational excitation is consistently smaller than in the corresponding gas-phase reactions (see Table 1 of ref. 4 for a summary of currently available data). This partial damping of the nuclear dynamics of the reactants by the surrounding solvent is indicative of coupling of solvent modes to the reaction coordinate, the local viscosity of the liquid environment, and the effects of solute-solvent complexes. Further progress in this field now requires development of methods which can observe

the ultrafast dynamics of the reacting species, the associated motions of the surrounding solvent molecules, and the flow of energy from the reactants into the solvent bath. The understanding that emerges from this field of reaction dynamics in liquids, and the techniques developed to observe transient reactive intermediates, should be valuable for mechanistic studies of reactions important in chemical synthesis.

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Summary statement

Experimental and computational studies of chemical dynamics in solution explore how a solvent modifies reaction mechanisms.

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